AOARD Report

Fabrication of Carbon Nanotube Channels on Three-Dimensional Building Blocks and Their Applications

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14. ABSTRACT
We report the synthesis SWNT-3DNs using a PE-CVD equipment and functionalization of the surface of SWNTs. A coaxial coating technique was introduced for improving the physical hardness of and the surface functionality of SWNT-3DNs that will extend the application fields of SWNT-3DNs. The basic application areas of SWNT-3DNs will be solar-cells, functional filters or sensors in micro-fluidic device.

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1. Introduction

Carbon nanotubes (CNTs) are the most attractive material in the fields of nanoscience and nanotechnology due to their chemical, physical and electrical properties. CNTs are being applied in various kinds of nano-devices such as transistors, electrodes, sensors and filters because of the semiconducting, metallic, optical and structural properties. To date, CNTs are mainly synthesized, grown and dispersed on two-dimensionally plat substrate. However, it is not easy to fabricate and manipulate CNTs on a particularly structured substrate for various applications. In the case of CNTs on planar substrates, it is hard to get high conductivity and sensitivity, because of physical disconnection and low surface areas due to randomly oriented two-dimensional structure. Three-dimensionally networked structure of CNTs with enlarging surface areas on pre-patterned substrate is ideal for device and sensor applications, but it needs to enhance the conductivity and sensitivity. The 3D network-structured CNTs can be used for a mechanical filteration of submicron components by controlling the size of network mesh with enhancement the mechanical strength.

Here, we report the syntheis SWNT-3DNs using a PE-CVD equipment and functionalization of the susface of SWNTs. And a coaxial coating technique was introduced for improving the physical hardness of and the surface functionality of SWNT-3DNs that will extend the application fields of SWNT-3DNs. The basic application areas of SWNT-3DNs will be solar-cells, functional filters or sensors in microfluidic device.

2. Approach and results

2-1. Coaxial coating of SWNT-3DNs with functional materials

The SWNT-3DNs are easily bundled and collapsed during the wetting and drying process because the capillary forces of the solution drew the suspended SWNT channels closer together as the solution dried and evaporated. This bundling effect of SWNT-3DNs is needed to avoid for SWNT-3DNs as nano-electrode with large active surface area.

Atomic layer deposition (ALD) appears to be one of the most versatile techniques for the well-controlled deposition of thin films on complex-shaped supports. The ALD is outstanding as it permits a precise control of the thickness of the deposited films at the subnanometer level while preserving their high homogeneity and conformality independent of the complexity of the substrate. However, the coating of CNTs with metal oxides of a well-defined and controllable thickness was not yet achieved. In this work we show that CNTs can be homogeneously coated on the outer and inner surfaces with a nanometric thick film of aluminum oxide to prevent collapsing of SWNT networks for various applications.

The Al_2O_3 thin films were deposited onto the SWNT-3DNs substrates using $[Al(CH_3)_3]$ and H_2O as ALD precursors. The Argon was served as both a carrier and a purging gas. The

trimethyl aluminum (TMA) and water were evaporated at 20 C. The cycle consisted of 1 s exposure to TMA, 5 s Ar purge, 1 s exposure to water, and 5 s Ar purge. The total flow rate of the Ar was 50 sccm. The Al_2O_3 thin films were grown at temperatures of 150–200^{o} C under a pressure of 300 mTorr.

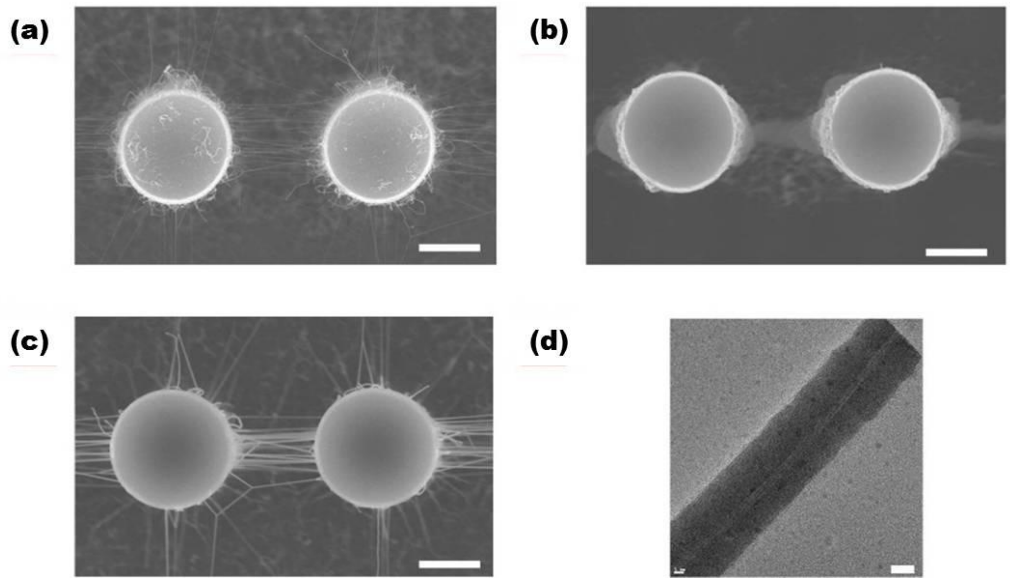

Figure 1. SEM images of (a)as-grown SWNT-3DNs and (b)collapsed SWNTs by the capillary force of a solution. (c)SEM and (d)TEM images of SWNT-3DNs coated by Al_2O_3.

Figure 1(b) shows that whole SWNTs collapsed during the wetting and drying process. CNTs coated with aluminum oxide are shown in Figure 1(c). In TEM image (Figure 1d) the darker regions on the outer walls of the CNTs correspond to the metal oxide layers deposited by the ALD process. The Al_2O_3 coating is uniform along the whole surface of the CNTs and shows approximately the same thickness of Al_2O_3 outer surface. Metal oxide coated SWNT-3DNs endured the capillary force, because the rigidity of metal oxide layer was increased from the untreated carbon nanotubes , so the SWNT-3DNs could stand without collapsing in solvent flow.

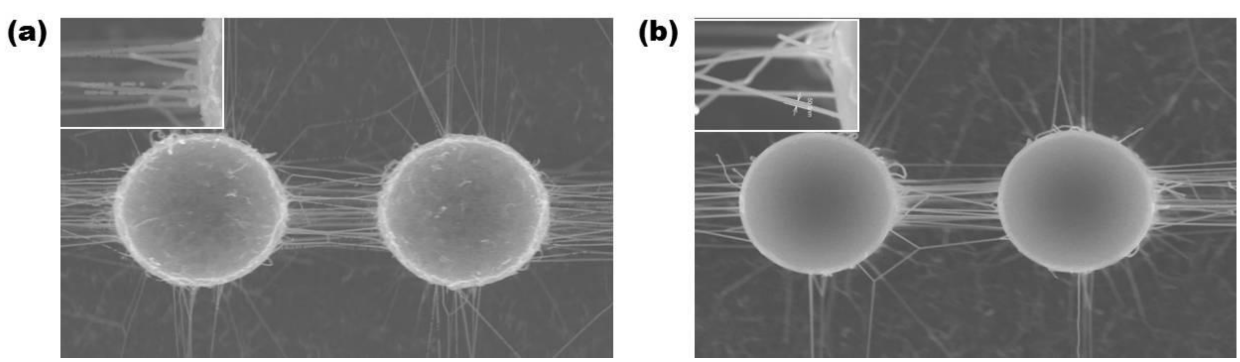

Figure 2. (a) SEM image of SWNT-3DNs coated with Al_2O_3 without UV-O_3 pretreatment. (b)SEM image of SWNT-3DNs coated with Al_2O_3 with UV-O_3 pretreatment, and it exhibits continuous Al_2O_3 ALD coating.

In Figure 2 SEM micrographs show the coating uniformity of aluminum oxide deposited on as-grown SWNTs. The measured thickness of deposited Al_2O_3 was 10 nm. Figure 2(a) shows a discontinuous Al_2O_3 coating on the surface of SWNTs. The formation of disconnected particles is attributed to the weak interactions between SWNTs and Al_2O_3 that leads to low nucleation rate and high surface diffusion rate of absorbed Al metal atoms. Clearly, a continuous and uniform coating of metal oxide on SWNTs cannot be achieved without UV-O_3 pretreatment. The functionalization of SWNTs with a UV-O_3 pretreatment reduces a probability of any nucleation inhibition. These results show that a nitro functional group specifically facilitates the reaction with the gas-phase ALD precursor molecules. This type of reaction is common in organometallic chemistry, and illustrates the significance of an appropriate ligand selection for functionalizing SWNTs for ALD coating purposes. In order to achieve continuous and uniform coating, the SWNT-3DNs should be pretreated by UV-O_3.

2-2. Fabricating SWNT-3DNs Using PECVD

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Unlike thermal CVD system, a plasma enhanced CVD (PECVD) system uses plasma to decompose a hydrocarbon gas such as C_2H_2, CH_4 and C_2H_4 etc. Thus, the synthesis of CNTs at low temperature is possible compare to the conventional thermal CVD method. But CNTs synthesized by PECVD have many defects and are short in size compared to those prepared by a conventional CVD system due to a chemical etching effect of the plasma ions. Plasma etching induces the breaking of SWCNT 3D network structure as shown in Figure 3. In order to fabricate SWNT-3DNs using PECVD, plasma etching effect should be decreased or avoided by certain treatments, because one or two graphene sheets of CNTs are easily broken by accelerated ions during PECVD process.

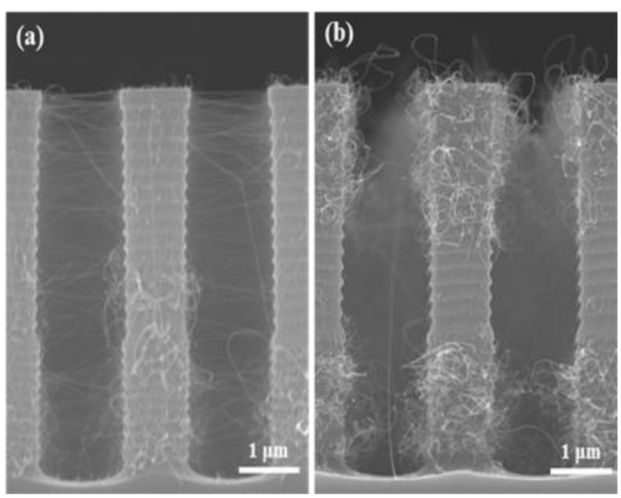

Figure 3. SEM images of SWCNT 3D network of (a) before plasma treatment and (b) after plasma treatment. Many SWCNT interconnects were broken by plasma.

The etching effects of plasma are dependent on the ion kinetic energy (E_i) and ion flux (J_i). According to other research group's study, E_i and J_i were related to pressure (P) and plasma power (V) as follows.

$$(1)\ E_i \propto V^{4/5}P^{-1/2}$$

$$(2)\ J_i \propto VP^{3/4}$$

As lowering plasma power, the plasma etching effect can be easily reduced. However, as lowering plasma power, ion flux also decreased. So it is not an effective method for reducing plasma etching effects during the process of SWNT-3DNs fabrication using PECVD.

Another method is for an inserting block layer to reduce ion kinetic energy. Blocking layer was effective in suppressing plasma etching effects, but ions cannot pass block layer. Although SWNT-3DNs network structure maintained as shown in Figure 4b, the CNT growth was interfered by a block layer (see Figure 4c).

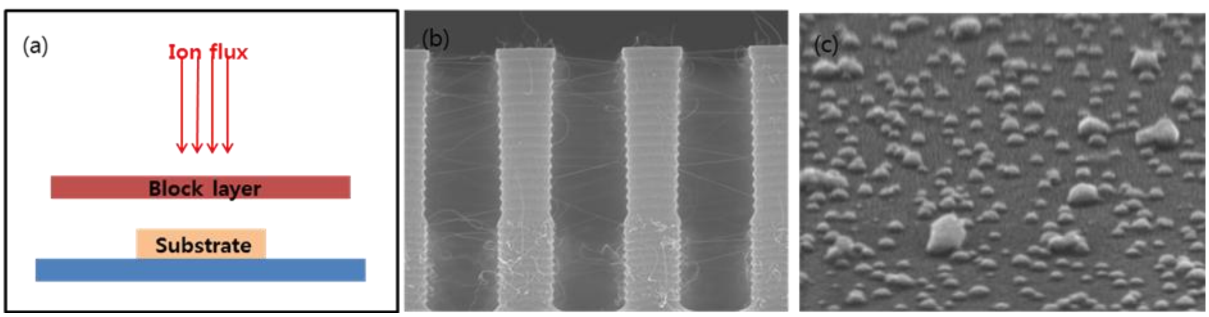

Figure 4. (a) Schematic of inserting block layer. (b-c) SEM images of block layer effects.

After this experiment, the mesh structure on the block layer was fabricated and inserted between a plasma source and a substrate to reduce the ion kinetic energy and increase the amount of ions for reached to the substrate. As making holes on the block layer, ions can pass through and reduce the ion kinetic energy at the same time. Without inserting a block layer with a mesh structure, CNTs were not interconnected between pillar structures (Figure 5b). However, CNTs formed interconnects well with this mesh blocking layer (Figure 5c).

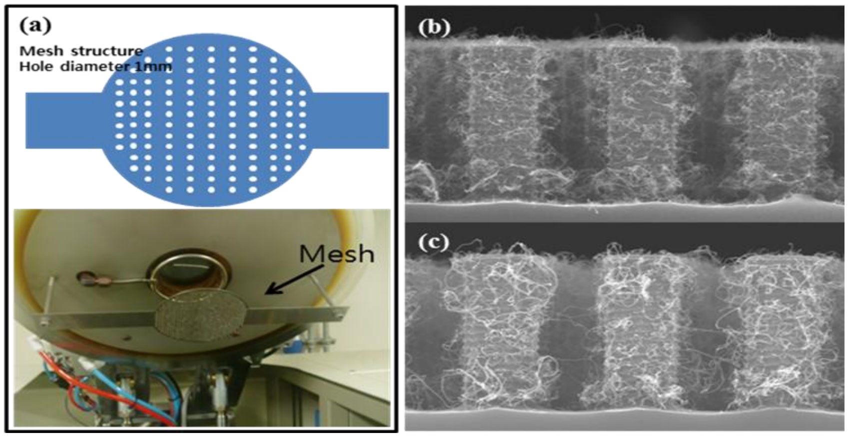

Figure 5. (a) Mesh structure inserted between a plasma source and a substrate. SEM images of (b) before and (c) after using a mesh during PECVD process.

However, the structure of MWCNTs synthesized by PECVD process was different from those prepared by the thermal CVD process. For the best network structure, the synthesis conditions are needed to be optimized. The number of CNT walls depends on the catalyst particle size. The size of catalyst particles is related to substrate temperature, annealing time and pretreatment plasma power during PECVD process. In our study, both annealing and pretreatment steps were conducted simultaneously to control the catalyst size effectively unlike as a conventional CVD process. The size of catalyst particles decreases by plasma etching effect. As a result, the CNTs network was formed like as prepared in thermal CVD system (Figure 6a). Although the density of CNT interconnects is lower than that of CNT interconnects prepared by thermal CVD, we anticipate the increase of the density of CNT interconnects by optimizing process parameters such as plasma power and pretreatment conditions.

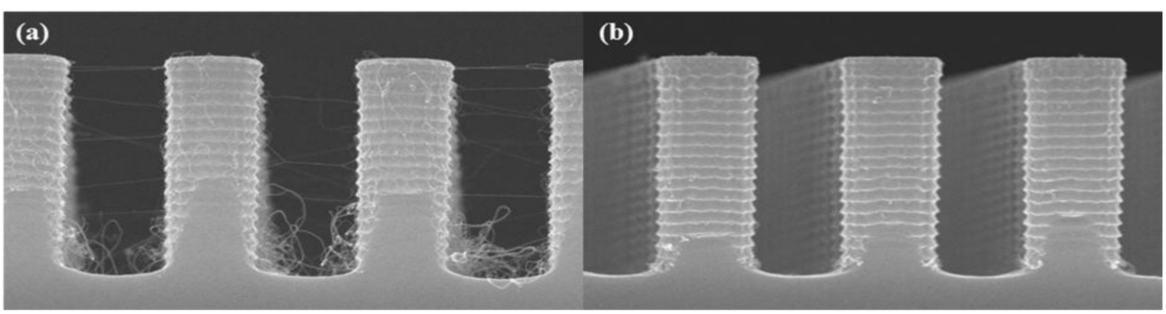

Figure 6. SEM images of CNTs network using combined annealing and pretreatment processes (a) with a mesh and (b) without a mesh inserted PECVD system.

2-3.Surface modification of CNTs using a plasma treatment

In order to use a CNT network structure for applications, the surface modification of CNT is very important. In general it is rather difficult to modify the surface of CNTs in the network structure without causing defects in CNT structure by chemical treatment. Plasma is a state of

matter similar to gas in which a certain portion of other particles are ionized. When plasma is treated on the CNTs, ions are accelerated into the surface. When ions collide onto the CNT surface, many defects are caused and ions form a new bonding at the same time on the surface of CNTs. In case of excessive high power plasma treatment, CNTs are easily destroyed by a plasma etching effect. In order to slightly modify the surface of SWCNT network, we used a mesh block layer to reduce the plasma etching effect. Although there are no distinct changes except for C_2H_2 treatment in three SEM images (Figure 7), we confirmed that new bonds were formed on the surface of SWCNTs by different gas sources through X-ray photoelectron spectroscopy (XPS) spectra as shown in Figure 8. XPS spectra showed the expected peaks of the graphitic C_{1s} (284.7 eV), N_{1s} (399 eV), O_{2s} (531 ev) and N_{2p} (890 eV), respectively. As shown in SEM and XPS data of C_2H_2 plasma, carbon materials are uniformly coated on both SWCNTs and Si surface by plasma polymerization. Plasma polymerization takes place in a low pressure, and the low temperature plasma is induced such as RF and DC. In case of our experiment, we maintained the pressure at 0.05 Torr and temperature at 25~35℃ using RF plasma. Under the NH_3 plasma treatment, the CNT surface is expected to incorporate nitrogen containing functional group such as amino, amide and imine. Amino groups on the surface of SWCNT are useful for various applications.

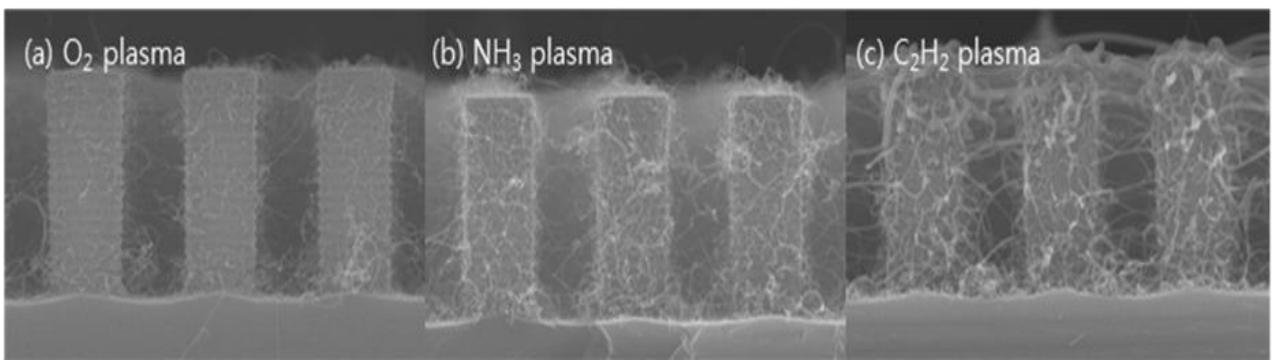

Figure 7. Surface modification of SWCNT 3D network structures with different types of gas plasma.

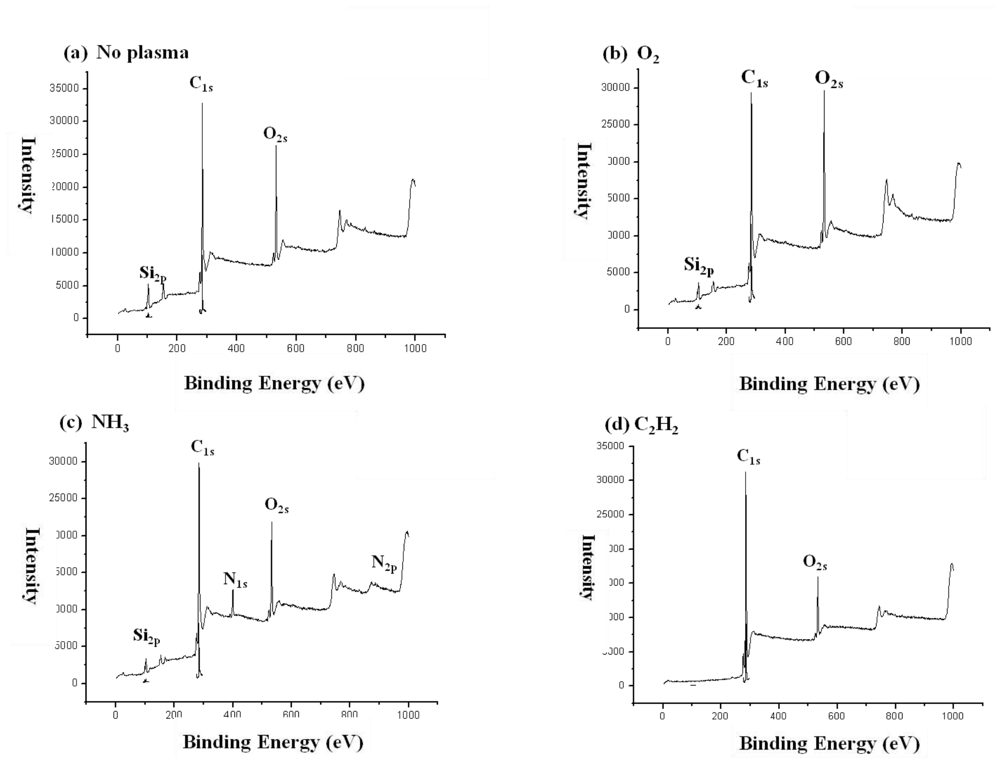

Figure 8. XPS spectra of surface modification of (a) SWCNT network using gas plasma. As gas source (b-d) new bond are formed on the surface of SWCNT. Especially (d) C_2H_2 plasma activated plasma polymerization on the all of surface.

2-4. Fabricating functional filters in microfluidic devices

SWNT-3DNs can be used as filters in microfluidic devices. The coaxial coating technique was applied onto the SWNT-3DNs to enhance their physical hardness because of the weakness of as-grown SWNT-3DNs in solvent flow. We investigated the basic performances of SWNT-3DNs as a filter or sensor on a simple micro-fluidic structure.

The microfluidic chip with a microfilter array based on 3D CNTs networks was connected to syringe pumps through capillaries and microfluidic fittings. Ethanol with aqueous fluorescent microspheres was injected into the inlet, and the flow rate was 0.02 µL/min (flow velocity was 40 µm/s). The fluorescent polystyrene microspheres (100 -500 nm in diameter) are used and the filtering performance of the microfilter and the microchannel flow were imaged using a fluorescence microscope and a CCD camera for monitoring a filtering performance of microfluidic chip by comparing fluorescent images of the upstream and downstream of pillar region (filter region).

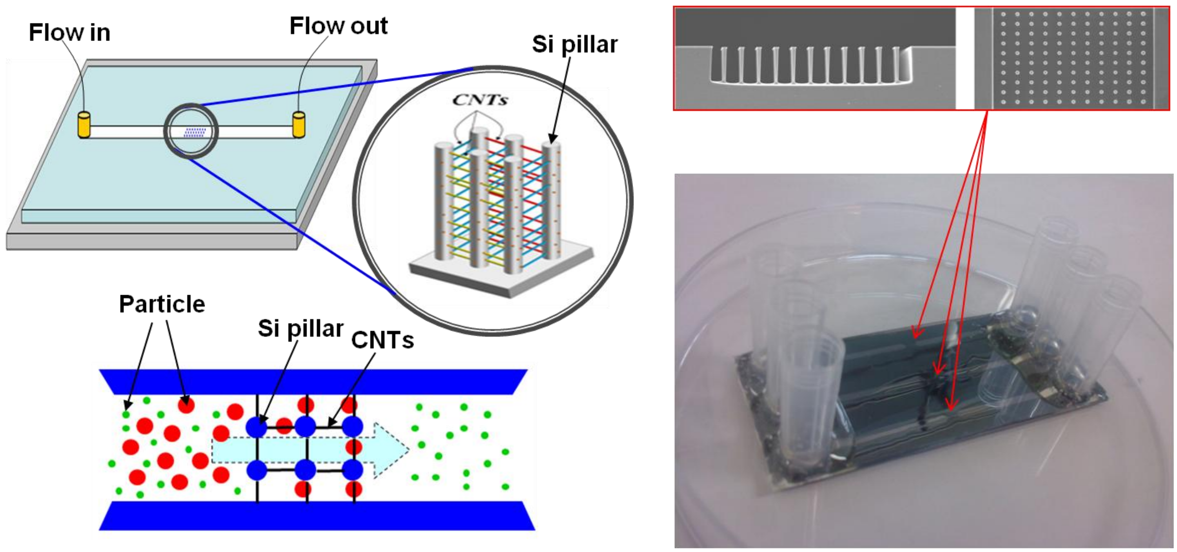

Figure 9. Schemes of SWNT-3DNs filter in microfluidic device (left), and a Si pillar structure fabricated for a filter in microfluidic device (right).

The SWNT-3DNs filter was evaluated for the successful removal of 100 nm PS particles from water (figure 10(b)). Most of CNTs filtration systems remove all PS particles independently from the size difference, but our filtering system showed a possibility of separating the different size of particles. The density of SWNTs interconnect was controlled by changing the distance of Si pillar to pillar. Figure 10(a) shows the lower density of SWNTs than that of SWNTs in 2um distance of pillar substrates (figure 10(b)).

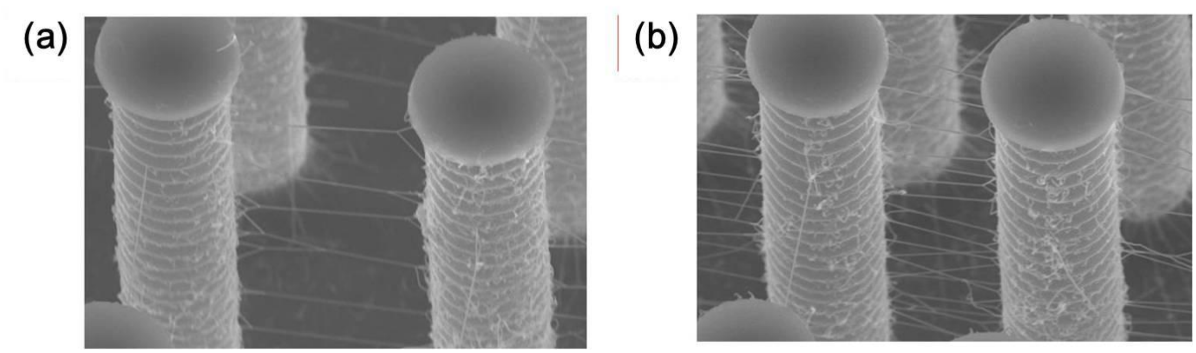

Figure 10. SEM images of SWNT networks on (a) a 5um-gap Si pillar substrate and (b) a 2um-gap Si pillar substrate with different density of interconnects

In order to demonstrate filtering capability of CNT elements we used a mixture of fluorescent beads that was moved through the channel using pressure driven flow. Figure 11 shows the fluorescent beads of 100 nm diameter concentrated in the SWNT-3DNs filter. Though CNTs surface is hydrophobic and coated with aluminum oxide in the SWNT-3DNs filtration chip, water can easily flow into the filter through a capillary action. It shows that SWNT-3DNs microfluidic chip can filter particles effectively.

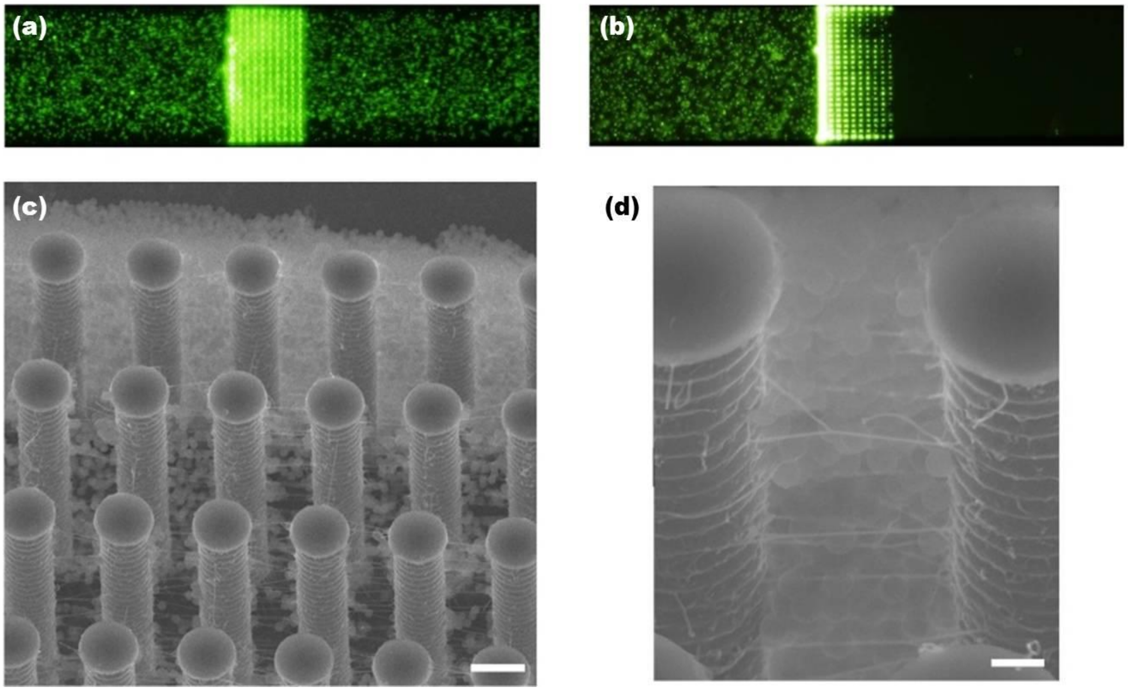

Figure 10. Removal of PS particles using SWNT-3DNs filter. (a) Image of PS particle flow on Si pillar substrate. (b) Image of PS particle filtrated by SWNT-3DNs. (c)-(d) SEM images of PS piles by SWNTs filtration system

3. Summary

We synthesized the high-density and uniform SWNT-3DNs on a micro-sized Si pillar template. Bundling and collapsing of SWNTs are prevented by surface modification with an ALD treatment. The density of SWNTs interconnects between pillars was well controlled by optimizing process parameters. We found that the plasma condition and catalyst size are two key factors of successful fabrication of SWNT-3DNs in PECVD system. The mesh block layer can effectively reduce a plasma etching effect, and both annealing and pretreatment steps are quite essential for 3D network structure fabrication.

4. Publication

1. Tae Jae Lee, Jeongeun Seo, Haiwon Lee, "Vertically aligned growth of single-walled carbon nanotubes on an Fe-Mo/MgO/Si substrate prepared by using a dipping method combined with an UV-ozone treatment", J. Korean Phys. Soc. 53 (2008) 3236.
2. Tae Jae Lee, Jungeun Seo, Haiwon Lee, Jung Woo Lee and Whikun Yi, "Fabrication of single-walled carbon nanotube three-dimensional networks inside the pores of a porous silicon structure" Carbon 48 (2010) 1473